

STABLE CARBON ISOTOPIC COMPOSITION OF INDIVIDUAL PRODUCTS FROM FLASH PYROLYSIS OF KEROGENS

By

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ABSTRACT

Recent analytical developments now allow determination of the stable carbon isotopic compositions of individual compounds eluting from a capillary gas chromatography column. This study describes compound-specific isotope measurements made on aliphatic hydrocarbon products from flash pyrolysis (800°C, 20s) of kerogens representing a range of depositional environments and ages. The carbon isotopic compositions of the major aliphatic pyrolysis products (*n*-hydrocarbons, acyclic isoprenoids and hopanoids), calibrated against those of deuterated *n*-alkane internal standards, were typically measurable to within $\pm 0.5\text{‰}$. The data show that for a given sample, *n*-alkenes and *n*-alkanes generally display rather similar values to one another irrespective of carbon number, suggesting a common (bio)polymeric origin. In several cases the average values also reflect the corresponding $\delta^{13}\text{C}$ TOC value, indicating that (for these samples) the *n*-hydrocarbons are derived from structurally important, or at least isotopically representative, components in the kerogen. Contrastingly, the isotope compositions of *n*-hydrocarbons varied substantially between samples (average values ranged from -33‰ to -14‰). Differences in isotopic composition were also apparent between the compound classes studied (e.g. hopanoids were isotopically lighter than the *n*-hydrocarbons).

The data obtained allow new deductions to be made regarding the source(s) of the precursor components in the kerogen and their importance in dictating the overall $\delta^{13}\text{C}$ TOC value. This technique is particularly useful for samples which gives rise to pyrolysis products whose structures are not sufficiently diagnostic to distinguish between biological sources. In these instances, isotopic data in combination with structural information, may prove invaluable in resolving separate carbon sources.

INTRODUCTION

Determination of the sources and composition of kerogen - the insoluble organic matter which is preserved in sediments and is ultimately responsible for accumulations of oil and gas - is a major goal in organic geochemistry. Kerogens represent a composite of remnants from a wide variety of organisms (algae, bacteria, higher plants) derived from both terrestrial and marine sources and reflect these differing inputs in a number of ways.

Of the approaches used in organic geochemistry flash pyrolysis has become widely accepted as a technique which can provide important and useful information on the structure and composition of kerogen and related geomacromolecules. Much progress has been made in understanding the pyrolysis mechanisms involved and in establishing precursor-pyrolysis product relationships for wide range of biomacromolecules and associated biochemicals. Pyrolytic markers have been established for the major biochemical precursors such as lignins^[1,2], aliphatic biopolymers^[3], polysaccharides^[4] etc. as well as materials of secondary origin such as sulfur-bound macromolecules^[5-8]. From such relationships the potential exists to reconstruct the proportions of different precursor components from the various biological sources which together comprise the kerogen. However, for a large number of sedimentary situations (particularly in diagenetically altered samples) the structure of the products generated upon pyrolysis are not sufficiently diagnostic to resolve individual sources.

Natural variations in the abundance of stable carbon isotopes (as a result of fractionation effects related to atmospheric and dissolved CO₂ equilibria and uptake) potentially may be used to distinguish between carbon sources according to depositional environment^[9] (e.g. freshwater *versus* marine) and trophic status^[10] (e.g. aerobic photoautotrophs *versus* methanotrophs). Applications based on this premise are now well established and, typically, the isotopic composition of the gross kerogen is measured (i.e. $\delta^{13}\text{C}$ TOC) for these purposes. However, since kerogens are usually comprised of a wide variety of components derived from potentially separate sources, $\delta^{13}\text{C}$ TOC represents a composite value. In order to resolve these separate contributions, the isotopic compositions of each of the individual constituents must be determined.

It has been clear for some time, therefore, that isotopic analyses on a molecular level have the potential to provide much more detailed information. As a result of several analytical developments, it is now possible to obtain stable carbon isotopic compositions of individual compounds eluting from a GC^[11-15]. Under conditions of optimal chromatography (i.e. baseline separation) and optimum sample size (individual peaks yielding 10⁻⁸ to 10⁻⁹ moles CO₂) a precision of $\pm 0.1\text{‰}$ is currently attainable^[14]. Previously the only practical alternative has been to isolate individual organic compounds using laborious fractionation and purification procedures so that they could be directly analyzed by isotope ratio mass spectrometry^[16,17]. With this newly available technology for on-line determination of the carbon isotopic composition of individual components eluting from a gas chromatograph it is now feasible to determine the isotopic compositions of individual pyrolysis products.

The combination of pyrolysis with compound-specific isotope analysis therefore holds tremendous possibilities for identifying and quantifying contributions from the various sources according to both structure (biochemical origin) and isotopic composition, with the ability to de-couple marine input from terrigenous sources representing a particularly important application. This paper describes preliminary results from a study designed to assess the viability and utility of this approach for the characterization of kerogens according to organic matter sources and depositional environment.

EXPERIMENTAL

Six sediments representing a range of depositional environments (marine, estuarine, lacustrine) and ages (Recent to Carboniferous) were chosen for analysis. Selected details are provided in Table 1. Kerogens were isolated from the sediments using established HF/HCl procedures and solvent-extracted prior to analysis.

Off-line flash pyrolysis experiments were performed on the isolated kerogens using a CDS 120 pyrolyser. Samples (1-5mg) mounted in quartz tubes were pyrolyzed (800°C, 20s.) using a coil pyroprobe in a stream of helium carrier gas. Volatile products were swept from a heated zone (200°C) and trapped in a glass U-tube immersed in liquid N₂. At the end of the pyrolysis experiment the products were retrieved from the U-tube by dissolution in a dichloromethane/hexane (1:1) and transferred to vials. Purified aliphatic hydrocarbon fractions

were isolated from the pyrolyzates by liquid chromatography on short columns (10cm x 5mm) containing activated silica and alumina using hexane as eluant.

Compound identification was achieved by conventional Gas Chromatography-Mass Spectrometry (GC-MS) using a Carlo Erba 4160 GC interfaced to Finnigan 4500 quadrupole MS (EI 50eV).

Compound-specific isotope analysis of the purified pyrolysis products was performed by Gas Chromatography-Combustion-Isotope Ratio Mass Spectrometry (GC-C-IRMS). The instrument set-up consists of a HP 5890 GC linked *via* a combustion interface to a Finnigan Delta-S isotope MS. The interface consists of three major components: a micro-combustion reactor, a non-cryogenic water extractor and an open split interface. As organic compounds elute from the GC they are combusted to CO₂ and H₂O in the reactor. Subsequently water is removed prior to entry into the mass spectrometer. The entire system is controlled by Finnigan ISODAT software. The stable carbon isotopic compositions of components of interest were calibrated against those of deuterated *n*-alkane standards co-injected with the sample. The isotopic composition of the standards was previously determined by conventional sealed-tube combustion. All isotopic compositions are quoted relative to PDB.

The bulk kerogens were also combusted and analysed separately to provide $\delta^{13}\text{C}$ TOC values by conventional isotope mass spectrometry using a Finnigan Delta-S mass spectrometer.

RESULTS

Masses 44 ($^{12}\text{C}^{16}\text{O}^{16}\text{O}$), 45 ($^{13}\text{C}^{16}\text{O}^{16}\text{O}$) and 46 ($^{12}\text{C}^{16}\text{O}^{18}\text{O}$) are simultaneously monitored during the GC-C-IRMS run. The ratio of m/z 45/44 is used to determine the carbon isotopic composition of the compound. A correction is made for ^{18}O -containing CO₂ from the intensity of m/z 46. Figure 1 shows m/z 44 mass chromatograms from GC-C-IRMS analysis of two of the kerogens studied. Since each compound is combusted to CO₂ on exiting the GC, the m/z 44 trace is analogous to a conventional FID signal. An expanded portion of a chromatogram showing variations in the m/z 45/44 ion current ratio (in addition to the m/z 44 trace) is presented in Figure 2. Compounds enriched in ^{13}C elute slightly earlier than the corresponding ^{12}C equivalent, and thus each peak is manifested in the m/z 45/44 trace as an inflection, the ^{13}C -rich component constituting the leading edge of the peak. The ratio of the magnitude of excursions away from the baseline by the ^{13}C (+ve inflection) and ^{12}C (-ve inflection) component gives the isotopic composition.

Four types of hydrocarbons were typically observed to dominate the chromatograms: *n*-alkenes, *n*-alkanes, acyclic isoprenoid and hopanoid hydrocarbons. Average isotopic compositions for these compound classes determined in the manner described above (summed over the appropriate carbon number range) are listed in Table 1 the six kerogens. Results from replicate analyses suggest that most values may be considered accurate to within $\pm 0.5\text{‰}$, however, in the worst cases (*i.e.* for samples which display complex chromatograms, or for components which are incompletely resolved) the uncertainty may be $\pm 1\text{‰}$ or more. Marine kerogens typically proved more difficult to study than lacustrine samples because of the more complex pyrograms they generate. In Figure 3 the stable carbon isotopic compositions of these pyrolysis products are plotted with respect to carbon number for each of the kerogens. The data show that for a given sample the isotopic compositions of *n*-alkenes and *n*-alkanes are generally rather similar (*i.e.* irrespective of carbon number). This finding suggests a common origin, consistent with a (bio)polymeric source. The average values of these components also, in several cases, reflect the corresponding $\delta^{13}\text{C}$ TOC value (*e.g.* Green River, Westfield), suggesting that they are derived from structurally important, or at least isotopically representative, components in the kerogen. In instances where isotopic compositions of the pyrolysis products do not closely match the $\delta^{13}\text{C}$ TOC, then alternative components must be considered. Regarding this point it should be borne in mind that the present investigation has only dealt with aliphatic pyrolysis products. The isotopic

compositions of normal hydrocarbons in the Messel kerogen pyrolyzate showed the greatest difference compared to the $\delta^{13}\text{C}$ TOC value, being up to 10‰ lighter. It has been proposed^[18] that both the kerogen and the normal hydrocarbon pyrolysis products from this shale derive predominantly from the cell-wall material of the freshwater alga, *Tetradron minimum*. Here, it is found that the hydrocarbon pyrolyzate is depleted in ^{13}C by ca. 5‰ relative to the total organic carbon (Table 1). Accordingly, the kerogen must contain ^{13}C -enriched components that do not yield aliphatic hydrocarbons on pyrolysis. It is required either that the visually recognized cell-wall material is isotopically inhomogenous or that some additional component is present. The alkane/alkene δ values observed in this work are very similar to those of acyclic hydrocarbons in extracts of the Messel Shale^[16,19].

The isotopic compositions of the various compound classes studied vary substantially from one sample to another. Average values for normal hydrocarbons range from ca. -33‰ (Messel shale) to ca. -14‰ (Westfield). With the exception of the Westfield kerogen, non-marine lacustrine samples (i.e. Messel and Green River kerogens) give lighter average isotope values than marine samples (Monterey, Peru, Spartina). The Westfield shale appears to represent a rather unusual and interesting case. The organic matter in the shale is almost exclusively comprised of the freshwater macroalga, *Botryococcus braunii*. The lack of isoprenoids in the pyrolyzate (Fig. 1) is also a characteristic feature of *B. braunii*-derived kerogens. Whilst the shale represents a freshwater lake deposit, the isotope values (both of the normal hydrocarbons and the TOC) are unusually heavy. This is likely to reflect low concentrations of dissolved CO_2 in the environment of carbon fixation. In such circumstances, many carbon-fixing organisms utilize special pathways (such as assimilation of HCO_3^-) for accumulation of inorganic carbon. Isotope effects associated with these largely irreversible processes are small in comparison to that of rubisco, and the resulting organic carbon is relatively enriched in ^{13}C .

Within-kerogen variations in isotopic composition are apparent between different compound classes generated from the samples studied. Isoprenoid hydrocarbons (when present) were found to vary significantly relative to the *n*-hydrocarbons (Fig. 1). In contrast, the hopanoids are in each case substantially lighter than both the TOC and *n*-hydrocarbons, with values as light as -50‰ recorded for hopanoids in the Messel kerogen pyrolyzate. These latter values show good agreement with those reported by Freeman *et al.*^[15] for hopanoids in solvent extracts of the same shale, indicating a bacterial (methanotrophic?) contribution to the kerogen.

CONCLUSIONS

Whilst this study contrasts geochemically very different kerogens, the results demonstrate that isotopic compositions may be readily determined for individual pyrolysis products by GC-C-IRMS. The data allow several new deductions to be made regarding the source of these components and their importance in dictating the overall $\delta^{13}\text{C}$ TOC value of the kerogen. The approach holds much promise, therefore, for assessing the various sources of biological remnants comprising the kerogen, and also for interpreting the overall TOC value in terms of these separate contributions.

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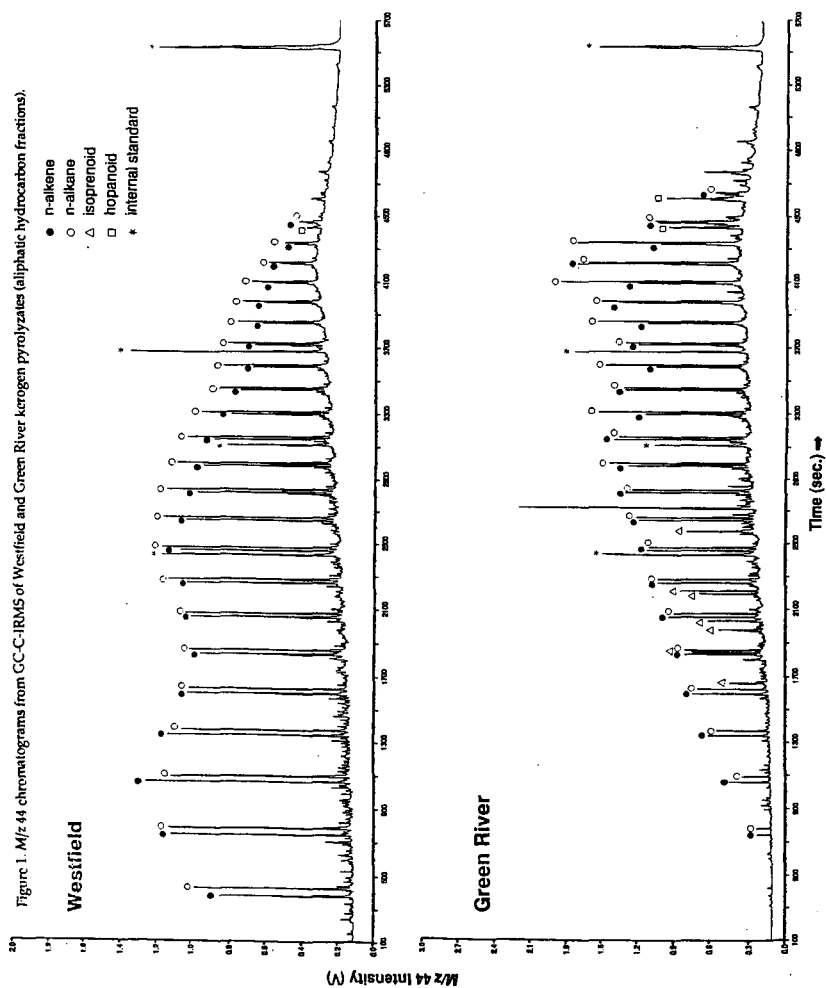
Table 1. Stable Carbon Isotope Data for Kerogens

Kerogen	Age	Env.	$\delta^{13}\text{C}$ Value (‰)				
			TOC*	Σene^1	Σane^2	Σisop^3	Σhop^4
Westfield, Scotland	Carb.	Lacustrine	-14.26	-14.71	-15.43	n.d.	-23.15
Messel, FRG	Eocene	Lacustrine	-27.69	-32.71	-33.13	-30.83	-45.47
Green River, UT, USA	Eocene	Lacustrine	-29.00	-28.99	-29.96	-31.27	-41.66
Peru, S. America	Contemp.	Marine	-20.47	-23.11	-23.82	-22.90	n.d.
Monterey, CA, USA	Miocene	Marine	-22.17	-23.95	-24.88	-24.64	n.d.
"Spartina", GA, USA	Contemp.	Estuarine	-18.54	-22.69	-23.30	-24.71	n.d.

*Determined by conventional sealed-tube combustion and MS.

¹n-alkenes; ²n-alkanes; ³isoprenoids; ⁴hopanoids.

n.d. = not detected



Peru Upwelling

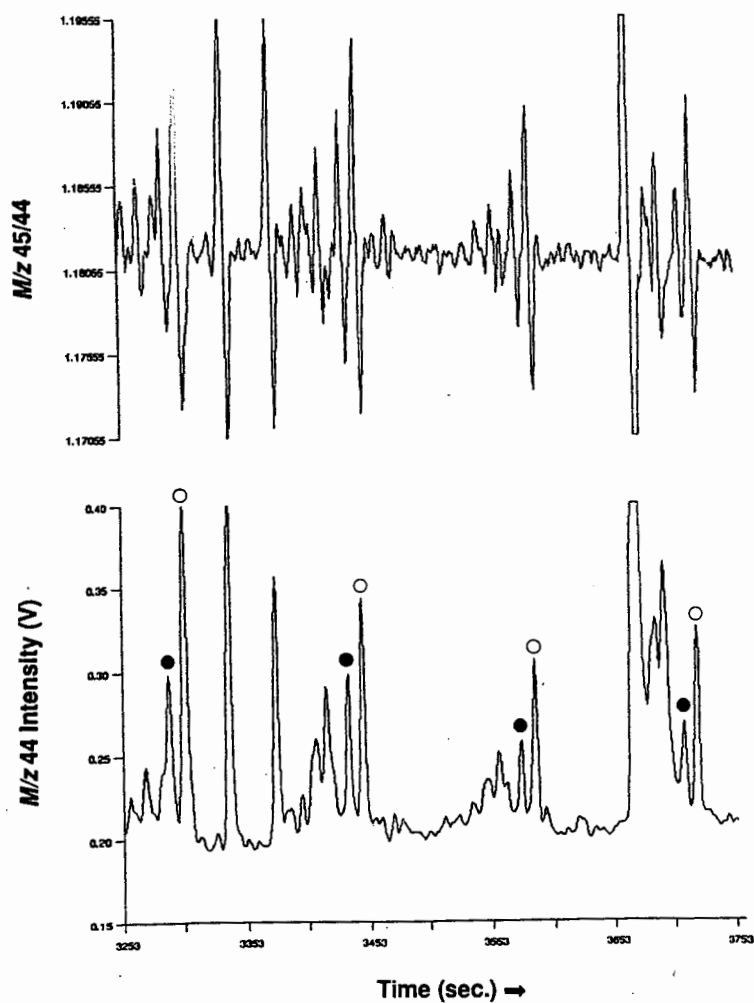


Figure 2. Partial chromatogram of m/z 45/44 ion current ratio (upper) and m/z 44 (lower) from GC-C-IRMS of Peru kerogen pyrolyzate (aliphatic hydrocarbon fraction). Open and closed circles represent n -alkanes and n -alkenes respectively.

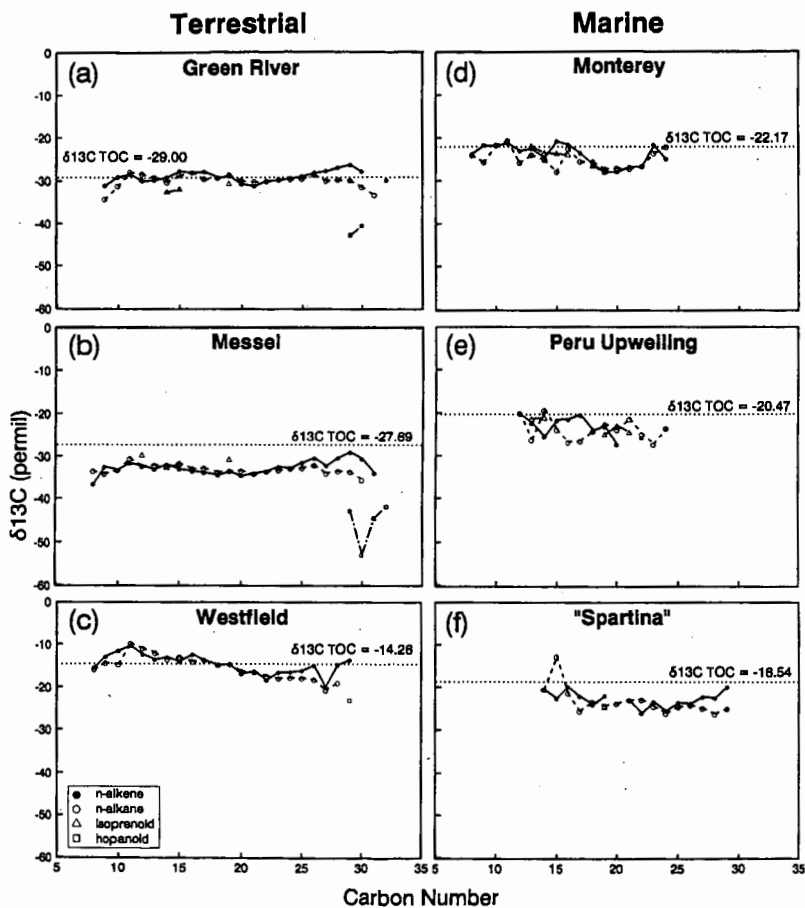


Figure 3. Plots of isotopic composition versus carbon number for different compound classes measured in the kerogen pyrolyzates.